

CLAIMS

1. A method of preparing unsaturated hydroxy fatty acids and esters thereof corresponding to general formula (Id):

Formula (Id)



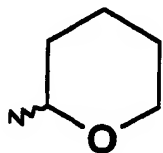
wherein $n = 1$ to 4 , $m = 2$ to 16 ,

$\text{R}_1 = \text{OH}$, Cl , Br , OR_3 in which R_3 is a straight or branched alkyl, alkenyl or alkynyl radical of 1 to 16 carbons or glycerol esters, optionally substituted by one or more atoms selected from the group consisting of carbon, nitrogen, sulfur and halogens,

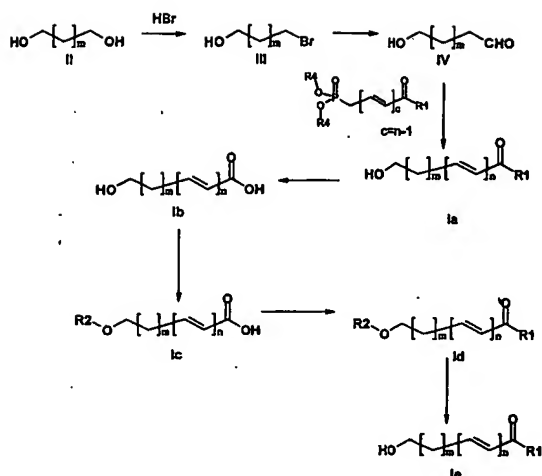
$\text{R}_2 = \text{H}$, $\text{SiR}'_1\text{R}'_2\text{R}'_3$ in which R'_1 , R'_2 and R'_3 can be identical or different from each other and are a straight or branched alkyl, alkenyl or alkynyl radical of 1 to 16 carbons or glycerol esters, optionally substituted by one or more atoms selected from the group consisting of carbon, nitrogen, sulfur and halogens,

or $\text{R}_2 = \text{C}-\text{Ar}_3$ with Ar representing an aryl radical optionally substituted by one or more atoms selected from the group consisting of carbon, nitrogen, sulfur and halogens,

or $\text{R}_2 =$ the tetrahydropyranyl of formula:



comprising causing a series of reactions according to a reaction diagram as follows:



wherein R_1 , R_2 , m and n have the same meanings as in formula Id.

2. The method according to claim 1, wherein a first step in the reaction diagram is a bromination, with an initial compound being a diol of formula (II).
3. The method according to claim 2, wherein the first step uses a solvent.
4. The method according to claim 3, wherein the solvent is selected from the group consisting of toluene, benzene, dimethylformamide, tetrahydrofuran, cyclohexane, heptane and petroleum ether.
5. The method according to claim 1, wherein a reagent used in a first step in the reaction diagram is selected from the group consisting of aqueous or nonaqueous HBr, Ph_3P, Br_2 , carbon triphenylphosphine tetrabromide and hydrobromic acid.

6. The method according to claim 1, wherein a second step in the reaction diagram is an oxidation in aldehyde of formula (IV) in the presence of an optionally cyclic, optionally anhydrous tertiary amine N-oxide and in the presence of DMSO.

7. The method according to claim 6, wherein the optionally cyclic, optionally anhydrous tertiary amine N-oxide is selected from the group consisting of N-methylmorpholine oxide, trimethylamine oxide, triethylamine oxide and mixtures thereof.

8. The method according to claim 1, wherein a third step in the reaction diagram is a Wittig-Horner reaction and a fourth step in the reaction diagram is a saponification reaction.

9. The method according to claim 8, wherein the Wittig-Horner reaction is carried out in the presence of triethylphosphonoacetate and potassium carbonate.

10. The method according to claim 1, wherein a fifth step in the reaction diagram is a specific protection of an alcohol functional group of the compound of general formula (Ib) obtained in a fourth step in the reaction diagram.

11. The method according to claim 1, wherein a fifth step in the reaction diagram is carried out in an enol ether in the presence of an acid catalyst.

12. The method according to claim 1, wherein a fifth step in the reaction diagram carried out with dihydropyran in the presence of PTSA (para-toluene sulfonic acid).

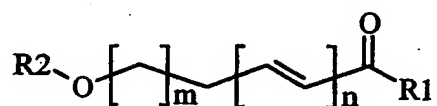
13. The method according to claim 1, wherein a product of formula (Id) obtained in a fifth step in the reaction diagram is subjected to a final deprotection to obtain the compound of general formula (Ie).

14. The method according to claim 1, wherein a product of formula (Id) obtained in a fifth step in the reaction diagram is used in an esterification reaction of the glycerol prior to undergoing final deprotection.

15. The method according to claim 13, wherein the deprotection is carried out in a methanol solution containing an acid catalyst.

16. The method according to claim 15, wherein the acid catalyst is PTSA.

17. A method of preparing unsaturated hydroxy fatty acids and esters thereof corresponding to general formula (Id):



wherein $n = 1$ to 4 , $m = 2$ to 16 ,

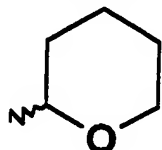
$\text{R}_1 = \text{OH}, \text{Cl}, \text{Br}, \text{OR}_3$ in which R_3 is a straight or branched alkyl, alkenyl or alkynyl radical of 1 to 16 carbons or glycerol esters, optionally substituted by one or more atoms selected from the group consisting of carbon, nitrogen, sulfur and halogens,

$\text{R}_2 = \text{H}, \text{SiR}'_1\text{R}'_2\text{R}'_3$ in which R'_1, R'_2 and R'_3 can be identical or different from each other and are a straight or branched alkyl, alkenyl or alkynyl radical of 1 to 16 carbons or glycerol

esters, optionally substituted by one or more atoms selected from the group consisting of carbon, nitrogen, sulfur and halogens,

or $R_2 = C-Ar_3$ with Ar representing an aryl radical optionally substituted by one or more atoms selected from the group consisting of carbon, nitrogen, sulfur and halogens,

or R_2 = the tetrahydropyranyl of formula:



comprising:

- a) brominating an initial diol of formula II:

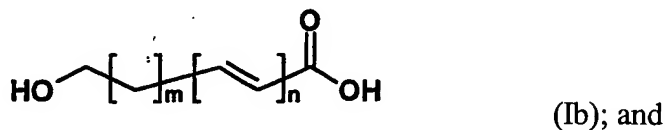


in an aqueous or nonaqueous solvent;

- b) oxidizing a bromide formed in step (a) in the presence of an optionally cyclic, optionally anhydrous tertiary amine N-oxide in the presence of DMSO to form an aldehyde of formula IV;

- c) subjecting the aldehyde formed in step (b) to a Wittig-Horner reaction;

- d) subjecting the product of step (c) to saponification to form a compound of general formula Ib:



- e) subjecting the compound of general formula (Ib) obtained in step (d) to a specific protection of an alcohol functional group in the presence of an acid catalyst.

18. The method according to claim 17, wherein the solvent is selected from the group consisting of toluene, benzene, dimethylformamide, tetrahydrofuran, cyclohexane, heptane and petroleum ether.

19. The method according to claim 17, wherein a reagent used in step (a) is selected from the group consisting of aqueous or nonaqueous HBr, $\text{Ph}_3\text{P}, \text{Br}_2$, carbon triphenylphosphine tetrabromide and hydrobromic acid.

20. The method according to claim 17, wherein step (b) is an oxidation of an aldehyde of formula (IV) in the presence of an optionally cyclic, optionally anhydrous tertiary amine N-oxide and in the presence of DMSO.

21. The method according to claim 17, wherein the Wittig-Horner reaction is carried out in the presence of triethylphosphonoacetate and potassium carbonate.

22. The method according to claim 17, wherein step (e) is carried out with dihydropyran in the presence of PTSA (para-toluene sulfonic acid).

23. The method according to claim 17, wherein a product of formula (Id) obtained in step (e) is subjected to a final deprotection to obtain the compound of general formula (Ie).

24. The method according to claim 17, wherein a product of formula (Id) obtained in step (e) is used in an esterification reaction of the glycerol prior to undergoing final deprotection.

25. A method of preventing or treating degradation of collagen comprising administering a therapeutically effective amount of a compound formed according to the method of claim 17 to a patient in need.

26. A method of preventing or treating degradation of collagen by bacterial collagenases during a bacterial infection comprising administering a therapeutically effective amount of a compound formed according to claim 17 to a patient in need.

27. A method of regenerating skin and ligaments comprising administering a therapeutically effective amount of a compound produced according to claim 17 to a patient in need.

28. A method of preventing or treating tumoral invasion comprising administering a therapeutically effective amount of a compound produced according to claim 17 to a patient in need.

29. A method of preventing or treating degenerative diseases having fibrinoid degeneration of collagen comprising administering a therapeutically effective amount of a compound produced according to claim 17 to a patient in need.

30. A method of reducing weight in a patient in need thereof comprising administering a therapeutically effective amount of a compound made according to the method of claim 17.